Polyimines from Terephthalaldehyde and Aliphatic Diamines. 6. Variable-Temperature CP-MAS ^{13}C-NMR Spectra of the Polyimine from 1,10-Diaminodecane

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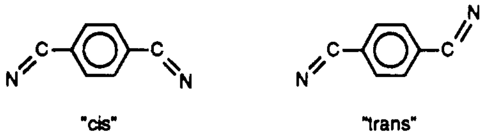
ABSTRACT: Four parameters are measured in the CP-MAS ^{13}C-NMR spectra of PI10, the polyimine from terephthalaldehyde and 1,10-diaminodecane. They are chemical shifts, proton and carbon $T_{1\rho}$ and T_{DD}, the time constant of dipolar dephasing. PI10 is a mixture of amorphous and crystalline phases, and the crystalline phase consists of an all-trans methylene spacer and two terephthalimine configurations:



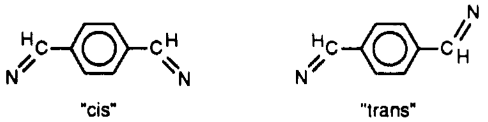
The chemical shifts of the protonated aromatic carbons and the proton and carbon $T_{1\rho}$ measurements indicate that phenyl flips occur at room temperature with a frequency below 67.5 kHz and that the frequency increases with temperature and exceeds 67.5 kHz at ca. 70–80 °C. $T_{1\rho C}$ measurements indicate that the dominant motion in the methylene spacer is an oscillatory one and that it exceeds the measuring frequency at ca. 90 °C. At the crystalline–smectic G transition temperature (T_{k-s} = ca. 107 °C), chemical shift measurements indicate that the "cis" structure melts into the amorphous background (the imine carbon) and that significant rotation starts occurring in the methylene spacer (trans–gauche upfield shifts of the methylene carbons). T_{DD} offers only qualitative information on the relative mobility of some carbons.

Introduction

Solid-state high-resolution NMR spectroscopy provides a wealth of information on polymer molecular structure and dynamics. New experimental techniques are being developed and applied to various systems at an impressive rate. Liquid crystalline polymers have been the subject of such studies for a relatively long time. Boeffel and Spiess[1] have reviewed the applications of ^{2}H-NMR and some 2D ^{13}C-NMR (mainly chemical shift anisotropy) techniques to obtain information on order and mobility in side-chain liquid crystalline polymers.

Simpler spectral approaches consist of running CP-MAS ^{13}C-NMR spectra as a function of temperature and monitoring changes in chemical shifts. These changes can then be assigned to various conformational and configurational motions taking place at different transition points of the liquid crystalline polymers. Where aliphatic main-chain spacers or aliphatic side chains are present, the methylene carbons usually show a typical trans–gauche upfield shift. This is due to the well-known γ-gauche effect.[2] Aromatic carbons also show nonequivalence in ordered structures, and a transition from a liquid crystalline to an isotropic state can be observed through changes in chemical shifts. Such studies were performed on polyesters,[3-5] polysiloxanes,[6] and a few rigid-rod polymers[7] and suggested on a polyether[8] and on a series of polyimines derived from terephthalaldehyde.[9] Apart from chemical shifts, various relaxation parameters (e.g., T_{1C}, T_{CH}, $T_{1\rho H}$, $T_{1\rho C}$) have been used to obtain information on relative mobilities and changes on mobility at the liquid crystalline transitions. Polyesters,[10,11] polyamides,[12] a poly(ester sulfide),[13] and a side-chain polymethacrylate[14] were studied.

In a series of papers we have shown that polyimines derived from terephthalaldehyde and aliphatic diamines are semicrystalline and melt into another relatively ordered phase before becoming isotropic.[9] The nature of the second phase depends mainly on spacer length.[15] PI10, the polyimine obtained from terephthalaldehyde and 1,10-diaminodecane, shows a smectic G phase in the temperature interval 107–143 °C on heating and 123–95 °C on cooling. This liquid crystalline range can be adjusted by using combinations of various diamines to produce copolymers.[16-18] CP-MAS ^{13}C-NMR spectroscopy was used to show that PI10 has two configurations of the terephthalimine in the crystalline state



and that in the amorphous fraction free rotation around the C(aromatic)–C(imine) bonds is supposed to take place. By comparing the spectra of PI10 in the semicrystalline state (as synthesized) and frozen from the liquid crystalline state, it was proposed that the first melting transition can be assigned to the onset on rotation around the C(aromatic)–C(imine) bond of the "cis" configuration (i.e., melting of this structure), while the second first-order transition on heating is assigned to the melting of the "trans" structures. Each of these structures melts into an amorphous, isotropic conformation. A possible nematic phase above the trans melting was postulated[9] but not observed, even in the copolymers. X-ray diffraction analysis of PI10 shows a very good correlation between the crystalline or liquid crystalline fraction and the amounts of cis and trans structures calculated from the NMR spectra.

This paper presents the results of the variable-temperature CP-MAS ^{13}C-NMR studies of PI10. Chemical shifts and relaxation parameters ($T_{1\rho H}$, $T_{1\rho C}$, and T_{DD}) are

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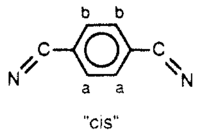
analyzed and correlated with the proposed molecular dynamics of this polymer.

Experimental Section

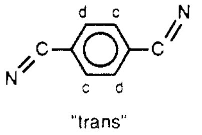
PI10 was synthesized as reported previously.[9] Variable-temperature CP-MAS ^{13}C-NMR spectra were run on a Bruker CXP-200 spectrometer operating at 50.307 MHz, equipped with a Doty probe. Spectra were collected each 10 °C from room temperature to 130 °C and then again at room temperature after heating. A new sample was used for each type of experiment. Chemical shifts were measured using the sharp signal at 132 ppm as an internal reference. Its chemical shift is unchanged over the temperature range used. The 90° proton pulse was 3.7 μs, and the cross polarization time was typically 2 ms. The delay betwen pulses was 5 s, and the decoupler was on for 0.09 s during carbon acquisition. $T_{1\rho H}$ was indirectly determined from the carbon resonances using the pulse sequence with increasing contact times proposed by Schaefer et al.[19] Contact times varied between 0.25 ms and up to 100 ms, when necessary. $T_{1\rho C}$ was measured using a pulse sequence in which the proton field is turned off for a variable time.[20,21] Delay times varied from 0.2 to 60 ms, with a proportionately larger number of short delay times. To estimate T_{DD}, the dipolar dephasing sequence proposed by Opella[22] was used and the dipolar dephasing time was varied between 0.25 and 50 μs.

Results and Discussion

A typical spectrum of PI10 is presented in Figure 1 together with the assignments. The imine and protonated aromatic carbon signals are complex and reflect the three types of structures present in the polyimine. The five signals of the protonated aromatic carbons have been previously assigned mainly on the basis of aromatic shielding effects.[9] Peak 4 is the aromatic nonprotonated carbon resonance for all the conformers. Peaks 5 and 8 (upfield side) arise from the protonated aromatic carbons "a" and "b" of the cis structure, while peaks 6 and 8 (downfield side) belong to the protonated aromatic carbons "c" and "d" of the trans structure, as illustrated below:



"cis"



"trans"

Peak 7 is the resonance of all protonated aromatic carbons in amorphous and/or freely rotating terephthalimine structures.[9]

The three imine carbon signals are tentatively assigned as follows: peaks 1 and 3 are assigned to imine carbons in the cis configuration. Peak 2 is assigned to imine carbons in the trans configuration and to imine carbons in the amorphous phase. The main reason for this assignment will be discussed later in the paper; it is based on the previously proposed thermal behavior of this polyimine.[9] At the first transition temperature on heating, the cis structures are melting, and this coincides with the disappearance of peaks 1 and 3. The trans and amorphous structures are postulated to be present above ca. 110 °C. Indeed, peak 2 is present above the first transition temperature, as will be shown later. Another proof for this assignment comes from the relaxation measurements which will be described later. As expected, both the proton and carbon relaxation time constants in the amorphous phase are much shorter than in the crystalline phase. Consequently, at relatively long delay times, the amorphous phase becomes completely relaxed and the spectrum corresponds only to the crystalline phase. Peak 7 disappears completely, as expected, but the signal of the imine carbons still contains all three parts, albeit with less intensity for peak 2. This means that all three peaks contain crystalline (cis and trans components); hence, the assignments proposed above must be correct.

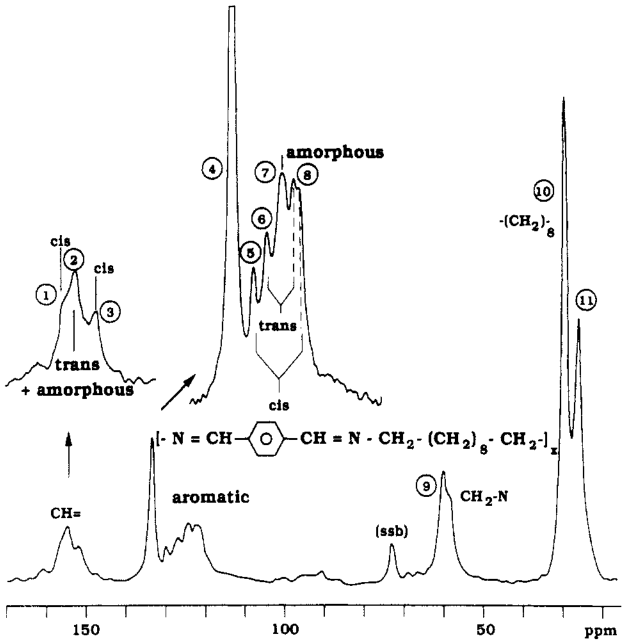


Figure 1. CP-MAS ^{13}C-NMR spectrum of PI10 with general assignments. More detailed assignments are discussed in the text.

Peaks 9–11 are methylene carbon resonances, as indicated on the figure.

Chemical Shifts. If the previous assignments are correct, the effects of the temperature should reflect the melting of cis at ca. 110 °C and the melting of trans at ca. 140 °C. Also, it was proposed by X-ray diffraction that the semicrystalline polymer has most of the methylene chains in a trans conformation, while in the liquid crystalline state some gauche conformations start occurring.[15] This should be noticeable in the aliphatic part of the spectrum. Above the smectic–isotropic transition temperature the sample becomes quite liquid. Due to obvious potential problems with cross-polarization, as well as with containing a liquid sample in a spinner designed for solids, the highest temperature at which spectra were run was chosen to be 130 °C. This is also the upper limit for the temperature controller.

Figure 2 shows spectra of the imine carbon at several temperatures. The relative intensity of the central signal—which was tentatively assigned to trans + amorphous structures—seems to increase steadily as the temperature increases, but the two side signals—assigned to the cis structure—are still visible in the spectrum run at 100 °C. At 110 °C the cis signals are not present, confirming that the crystalline–smectic G transition is associated with a melting of the cis configuration. The apparent decrease in the intensity of the cis signals may be related to different efficiencies of cross-polarization as a function of temperature for the three types of structures.

Figure 3 shows what happens to the aliphatic carbon signal as the temperature is raised. The spectrum is unchanged between 40 and 100 °C. At 100 °C, obvious upfield shifts start to appear, and they predominate at 110 °C. As the temperature reaches 120 °C, the two initial aliphatic signals are not present anymore; they have been replaced by two other signals at higher fields. The spectrum at 130 °C is identical to that at 120 °C. This upfield shift of the methylene carbons is due to the trans–gauche rotations which start occurring in the sample as

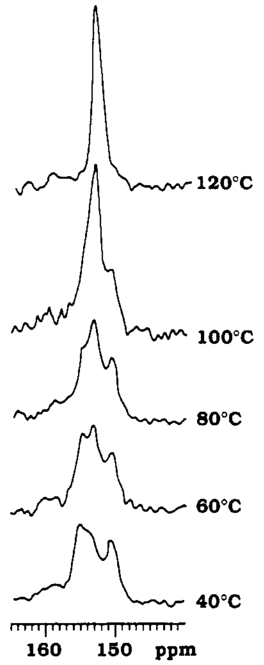


Figure 2. CP-MAS ^{13}C-NMR spectra of the imine carbon signal recorded at the temperatures indicated on each spectrum.

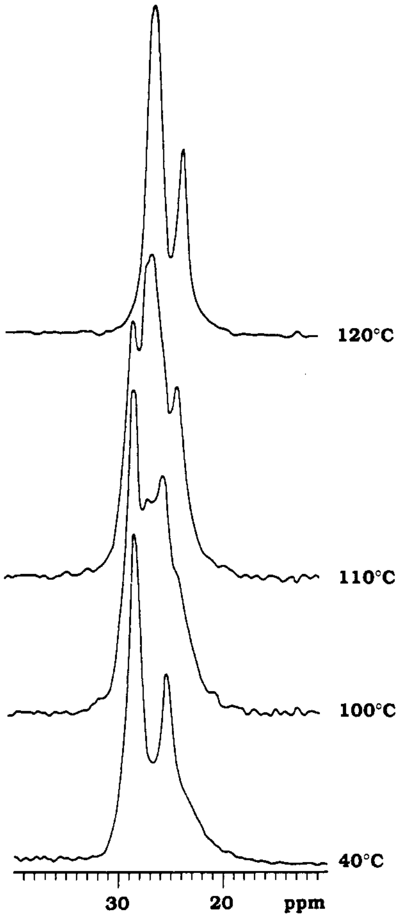


Figure 3. CP-MAS ^{13}C-NMR spectra of the internal methylene carbons recorded at the temperatures indicated on each spectrum.

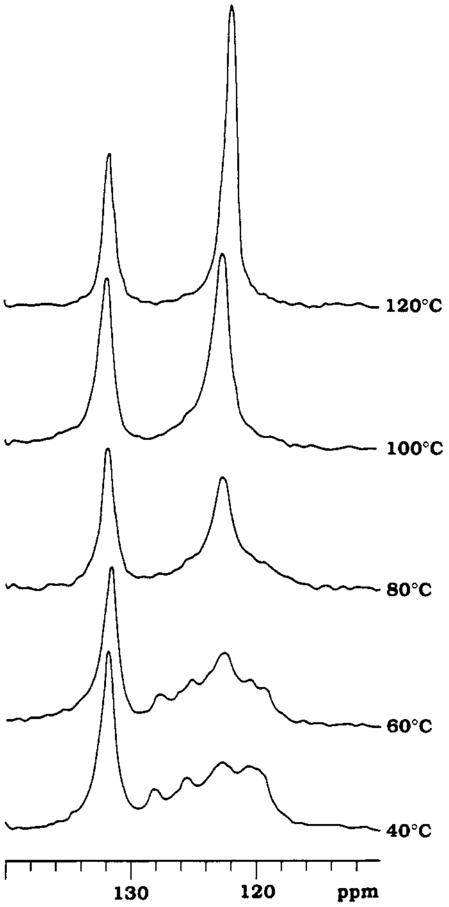


Figure 4. CP-MAS ^{13}C-NMR spectra of the aromatic carbons recorded at the temperatures indicated on each spectrum.

the crystalline–smectic transition is being reached (107 °C estimated by DSC). According to models built to fit the X-ray parameters,[15] the smectic G phase contains on average between one and two C–C bonds in the gauche conformation. The actual chemical shift observed in the spectra should thus be a weighted average of the shifts for all carbons in the methylene spacer. It must be emphasized that the spectra are not quantitative. Another fact to consider is that it takes ca. 2 h to run a spectrum for chemical shifts and that during this time the sample is obviously not in equilibrium, as it goes through the transition. This is the explanation for the gradual change from the crystalline conformation to the dominant smectic conformation of the methylene spacer. Above the smectic–isotropic transition, a more gauche conformation is introduced in the methylene chain. This was verified on a copolymer containing 90 mol % of this decamethylene spacer and 10 mol % of a trimethylene spacer. Both transitions are depressed in the copolymer due to the increased disorder, and the smectic–isotropic transition occurs at ca. 130 °C.[16] Spectra run on this copolymer at 130 °C clearly show a subsequent upfield shift of the two aliphatic carbon signals starting to occur around the second transition.[23] This confirms both the assignment of this upfield shift to trans–gauche rotations and the fact that the smectic phase contains a limited amount of gauche conformations on average.

Finally, the aromatic carbon signals are presented in Figure 4 as a function of temperature. Here too, it was expected that the cis signals would collapse into the central signal of the protonated carbons after 110 °C but that the trans signals would still be present in the liquid crystalline state. This is not what Figure 4 shows, however. Both the cis and trans signals collapse into the central signal at ca. 70–80 °C. This central signal becomes narrower as the temperature increases. There is no change in the nonprotonated aromatic carbon signal.

The reason for the nonequivalency of the protonated aromatic carbons of the cis and trans conformations is that they belong to rigid structures and that the phenyl flips, which would average their chemical shift, must be slow on the NMR time scale. There are two possible

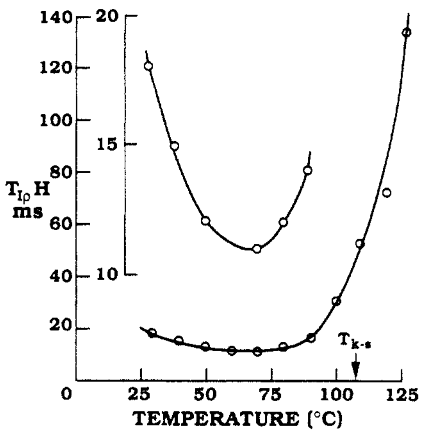


Figure 5. $T_{1\rho H}$ as a function of temperature for PI10.

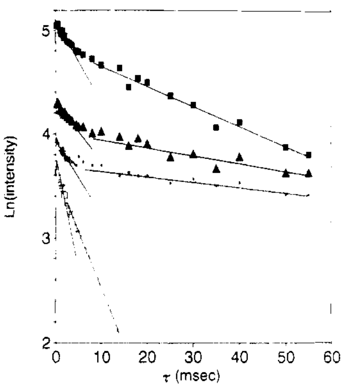


Figure 6. Magnetization decay for (■) signal 10 (Figure 1), (▲) signal 5 (Figure 1), (*) signal 4 (Figure 1), and (□) signal 7 (Figure 1). Spectra were obtained at room temperature.

explanations for the single peak of the protonated aromatic carbons above 80 °C. The first is that the phenyl flips rate increases as the temperature increases and that at 80 °C it becomes fast on the NMR time scale. The second is that the cis and trans structures start rotating freely ("melt") at this temperature. This second explanation is contradicted by both the DSC data[9] and the imine carbon signal behavior. Some X-ray data also suggest that the trans structure is still present in the smectic phase.[15] Relaxation parameters will also confirm that the first explanation is the correct one.

Proton $T_{1\rho}$. $T_{1\rho H}$ is one of the relaxation time constants which describes spin diffusion within a sample. For a homogeneous polymer all carbon signals will relax with the same $T_{1\rho H}$. Consequently, $T_{1\rho H}$ can be used to analyze the phase structure of polymer blends. Typical values of $T_{1\rho H}$ for polymers are in the range of a few milliseconds, which probes domains on a nanometer scale. This is more intimate than the information provided by glass transition measurements. There are only a few instances when $T_{1\rho H}$ can be measured separately for crystalline and amorphous domains. This can be done if the two phases generate separate resonances or if the difference between the two $T_{1\rho H}$ is at least 1 order of magnitude, so that the signal decay is clearly biexponential. Both conditions are present for polyethylene, for example.[24]

In the case of PI10, only the central signal of the protonated aromatic carbons can be assigned to belong exclusively to the amorphous phase below 70 °C. All other signals are resonances of carbons in both crystalline and amorphous phases. Measurements of $T_{1\rho H}$ for the amorphous signal are approximate, because this signal is not resolved enough to be free of influences from the crystalline phase. However, the $T_{1\rho H}$ of the amorphous phase is consistently lower than the average $T_{1\rho H}$ measured on all the other signals by ca. 30%. This confirms that there are two phases in PI10 and that the spin diffusion in these two phases is slightly different. No quantitative information can be obtained here for the reasons mentioned above.

There are a few factors which affect the $T_{1\rho H}$ value. In the case of PI10 one can assume that changes in proton density are rather minor when the temperature is increased, except at the liquid crystalline transition temperatures. Consequently, changes in $T_{1\rho H}$ with the temperature are most likely the result of motional changes. Figure 5 shows the variation of $T_{1\rho H}$ as a function of temperature. The value measured on all signals except the central protonated aromatic carbons was taken to be the average $T_{1\rho H}$.

The variation of $T_{1\rho H}$ with temperature shows a minimum around 70 °C. Below the minimum the sample is "solid" from the NMR point of view; i.e., the motions which are associated with $T_{1\rho H}$ (in the kilohertz range) are relatively slow. Above the minimum the sample behaves as a "liquid", and the $T_{1\rho H}$ increases as the temperature increases. The slope of the curve jumps significantly above the crystalline-to-smectic transition ($T_{k\text{-}s}$ in the figure), which is expected due to a significant rise in the overall mobility of the sample upon melting the cis structures. Figure 5 tells us that at ca. 70 °C a barrier for a certain motion is overcome. This correlates well with the data in Figure 4, where the phenyl flips start becoming fast at about the same temperature. Hence, one can conclude that the dominant motion for $T_{1\rho H}$ is phenyl flips and that its frequency probably exceeds the measuring frequency (67.5 kHz) at ca. 70 °C. These flips do not affect the crystalline structure; i.e., the phenyls are rotating within the crystals or within the smectic phase without disrupting any of them. There is no indication of any thermal effects of these flips in the DSC, which is expected, because DSC is not sensitive to changes in frequency.

Carbon $T_{1\rho}$. It is well-known that the decay of magnetization which gives $T_{1\rho C}$ is rarely exponential for polymers. This is usually explained by a multiplicity of relaxations for the various structures of a polydisperse polymer.[20] Examples of such decays are presented in Figure 6. They have been fit with two exponentials. Normally, for all carbons at all temperatures, when a clear biexponential decay is present, the slow components comprise about 90% of the carbons. No clear variation of this percentage with temperature could be established. The estimation of the initial slope, sometimes called the average relaxation time constant $\langle T_{1\rho C}\rangle$, has a higher experimental error than the estimation of the long $T_{1\rho C}$. Taking into account this higher error, the general features of changes in $T_{1\rho C}$ with the temperature are very similar for both the slow component and for the average. Hence, the discussion of the temperature variations will be illustrated with the slow component.

A comparison of the actual values of $T_{1\rho C}$ at room temperature gives an idea about relative mobilities of various carbon atoms. The slowest relaxation is exhibited by the nonprotonated aromatic carbons ($T_{1\rho C}$ = 270 ms). The mechanism of relaxation for carbons which do not have attached protons is unknown, but the fact that these carbons have the longest $T_{1\rho C}$ confirms the role of the adjacent protons in this relaxation. This means that it is reasonable to assume that here, too, spin–lattice is the dominant relaxation process and that it reflects the spectral density at 67.5 kHz (corresponding to the 3.7-μs proton

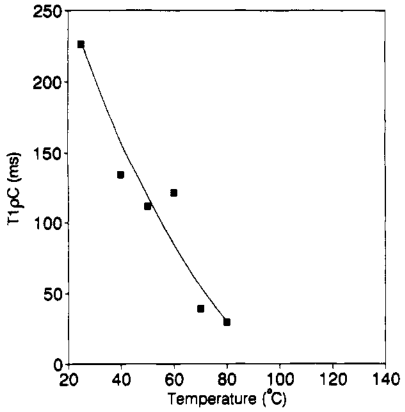


Figure 7. $T_{1\rho\mathrm{C}}$ for peak 5 (Figure 1), one of the cis protonated aromatic carbon signals, as a function of temperature.

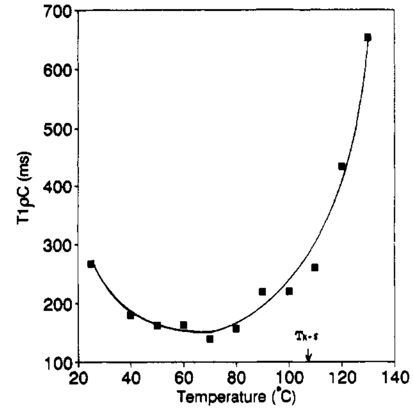


Figure 8. $T_{1\rho\mathrm{C}}$ for peak 4 (Figure 1), the nonprotonated aromatic carbon signal, as a function of temperature.

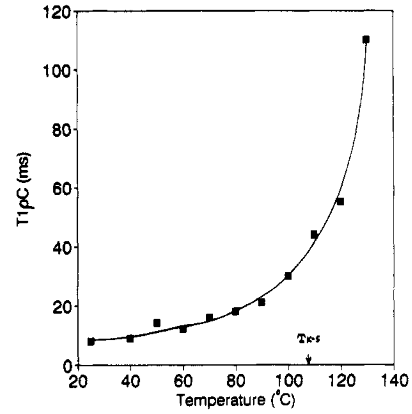


Figure 9. $T_{1\rho\mathrm{C}}$ for peak 7 (Figure 1), the amorphous protonated aromatic carbon signal, as a function of temperature.

pulse). Next, there are the protonated aromatic carbons and the imine carbons. In this case, a clear distinction between most of these signals is not possible. Signals 1–3 in Figure 1 are partly overlapped, which signifies that their decays interfere with each other. The two cis imine carbons appear to relax with a 115-ms time constant, while the central signal (2), assigned to the trans and amorphous components, has a $T_{1\rho\mathrm{C}}$ of 100 ms. Significant overlap exists for the protonated aromatic carbons as well, but signal 5 (Figure 1) may generate a value closer to the truth ($T_{1\rho\mathrm{C}}$ = 230 ms; fairly high, which is to be expected for rigid carbons). The other two rigid carbon signals (6 and 8—signal 8 has one cis and one trans component) relax with a time constant of 115 ms.

Next, with decreasing $T_{1\rho\mathrm{C}}$ values, are the methylene carbons with 60 ms (for the α-methylene), 70 ms (for the main $-CH_2-$ peak), and 55 ms (for the γ-methylene). Even though these methylene spacers are keeping their all-trans conformation within the crystalline structure, and—to some extent—even in the smectic phase, some motions are allowed. Such oscillations, for instance, may be the explanation for the relaxation mechanism. Finally, the fastest relaxing are the amorphous protonated aromatic carbons. This is not surprising, because signal 7 is the only signal arising exclusively from the amorphous phase of PI10. Its $T_{1\rho\mathrm{C}}$ is 10 ms.

Variable-temperature measurements of $T_{1\rho\mathrm{C}}$ are very important in order to find out on which side of the minimum is room temperature. The variation of $T_{1\rho\mathrm{C}}$ with temperature follows a few patterns for different carbons:

The cis and trans protonated aromatic carbons (peaks 5, 6, and 8 in Figure 1) are on the low-temperature side of the $T_{1\rho\mathrm{C}}$ minimum. Figure 7 illustrates the variation of $T_{1\rho\mathrm{C}}$ for peak 5 as a function of temperature. Peaks 6 and 8 show similar decays; only the actual values of $T_{1\rho\mathrm{C}}$ are different. Peak 5 ceases to exist after 80 °C, as was demonstrated in Figure 4. The dramatic decrease in $T_{1\rho\mathrm{C}}$ in this range of temperatures for the aromatic carbon signals associated with the crystalline phase correlates well with the previous results. Figure 7 suggests that the dominant mechanism of relaxation for these carbons is related to the frequency of phenyl flips. This frequency increases with temperature and becomes fast at ca. 70–80 °C (as the collapse of the peaks in Figure 4 and the minimum of the $T_{1\rho\mathrm{H}}$ curve in Figure 5 assess). With the frequency increase, the carbons relax faster and faster. Above 80 °C, these carbons belong to peak 7 (Figure 1).

The nonprotonated aromatic carbons (peak 4 in Figure 1) show a typical temperature dependence with a minimum, as illustrated in Figure 8. This signal includes crystalline and amorphous components, and its relaxation mechanism is not known, in the absence of any protons attached. However, it is clear that at room temperature the $T_{1\rho\mathrm{C}}$ is on the low-temperature side of the minimum and that the relaxation rate increases as the temperature (and the motion) increases. The minimum is at ca. 70 °C, which suggests that the phenyl flips may play a significant role in relaxation. Above the minimum the relaxation rate decreases, because the frequency of the dominant motion is already greater than 67.5 kHz. A great increase can be noticed above $T_{\mathrm{k-s}}$, as expected upon melting of one of the components.

The amorphous protonated aromatic carbons (peak 7 in Figure 1) are aleady moving fast at room temperature. The curve presented in Figure 9 shows that $T_{1\rho\mathrm{C}}$ is on the high-temperature side of the minimum at room temperature and that it increases steadily with the temperature. The increase becomes steeper at ca. 90 °C. Starting at this temperature, the signal becomes a combination of all protonated aromatic carbons, crystalline and amorphous.

The trans and amorphous imine carbons and all the aliphatic carbons (peaks 2 and 9–11) show the same shape of the $T_{1\rho\mathrm{C}}$ curve as a function of temperature. As an example, Figure 10 shows the imine carbon. The $T_{1\rho\mathrm{C}}$ is relatively insensitive to temperature until ca. 60 °C. Above this temperature, the relaxation of all these carbons becomes faster and reaches a maximum (minimum $T_{1\rho\mathrm{C}}$) at ca. 90 °C. Then the relaxation rate decreases at a great pace. The fact the relaxation is faster as the temperature increases confirms that the dominant mechanism of relaxation for these carbons has to be motional. The minimum $T_{1\rho\mathrm{C}}$ is not related to the phenyl flips rate for these carbons, and this is to be expected, as none of these carbons is aromatic. The motion which affects this relaxation is probably oscillatory, and the frequency or

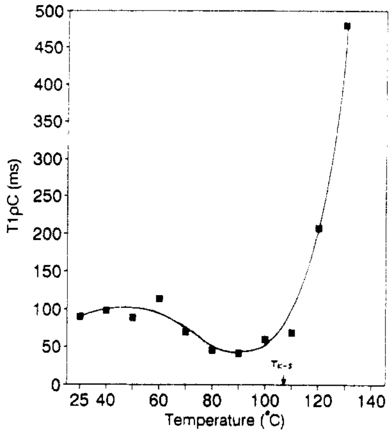


Figure 10. $T_{1\rho C}$ for peak 2 (Figure 1), the trans and amorphous imine carbon signal, as a function of temperature.

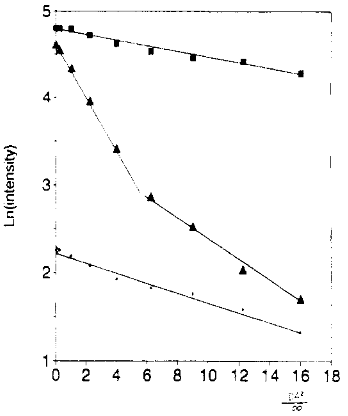


Figure 11. Magnetization decay for (■) signal 7 (Figure 1), (▲) signal 10 (Figure 1), and (*) signal 2 (Figure 1). Spectra were obtained at 90 °C.

amplitude of these oscillations increases with the temperature until they exceed the spectral density at 67.5 kHz. From then on (above 90 °C), these carbons relax slower and slower at this frequency.

Signals 1 and 3 have not been included in this discussion, because the error in measuring these partly overlapped signals is rather high. The shape of the curve for signal 1 in Figure 1 (the cis imine carbons) is similar to the shape presented in Figure 7, except that it has a minimum at ca. 90 °C, as the corresponding trans and amorphous imine carbons do (Figure 10). This shape is consistent with the previous analysis. Signal 3 in Figure 1, however, shows too much scatter to be discussed.

Dipolar Dephasing. Dipolar dephasing is used mainly as an assignment tool. Typically, after ca. a 60-μs delay, most of the methylene and methine carbon signals disappear from the spectrum. Nonprotonated carbons remain because they are weakly coupled to protons. The methyl carbons also remain, but for a different reason, usually related to their higher mobility. Grant et al.[25] established a relation between the magnetization of a certain carbon and the delay time, assuming the decay process to be exponential. The time constant for the decay can then be retrieved from the inverse negative of the slope in the ln(intensity) versus (delay)^2 plot. T_{DD} is the square root of half of the inverse negative slope. This relation is valid for strongly coupled carbons, such as methylene and methine carbons. For weakly coupled carbons, a simple exponential relation as a function of the delay time yields T_{DD} from the negative inverse slope of the intensity decay.

Very few applications of these relations have been attempted in the literature. The most notable is an analysis of the polyethylene[26] and the conclusion that there are different crystalline and amorphous phases from the biexponential decay of the intensity versus the delay time. As a general rule, there are many qualitative observations of more or less intense signals at various decay times in the Opella sequence,[22] but not many quantitative interpretations.

Figure 11 illustrates the decay curves for three carbon signals at 90 °C as an example. The slowest relaxing is the amorphous protonated aromatic carbon signal, followed by the central imine carbon signal. The signal corresponding to the main methylene carbon signal has an obvious biexponential decay, but both slopes indicate a faster relaxation rate than for the two other signals in Figure 11. As a general rule, a faster relaxation (shorter T_{DD}) is taken as an indication of stronger carbon–proton coupling, hence, a more rigid structure. Increased motion weakens this coupling and hence decreases the relaxation efficiency. In Figure 11, the amorphous protonated carbons relax slower, indicating a higher mobility, as expected from the previous findings. The methylene carbons have more protons attached and generate at all temperatures an apparent biexponential decay. This may be interpreted as a consequence of the two phases (all methylene resonances arise from the crystalline and amorphous phases as well) or as a consequence of a more complicated relaxation mechanism.

Analysis of T_{DD} values for various carbons as a function of temperature does not produce very consistent and interpretable results. Some trends are obvious. For example, Figure 12 illustrates the variation of T_{DD} for the γ-methylene carbons (signal 11 in Figure 1) and the percentage of the slow component as a function of temperature. This peak has a fast relaxing component for which T_{DD} seems to be independent of temperature and a slower relaxing one. For the slower component T_{DD} increases as the temperature increases, suggesting that a motional interpretation of the relaxation is reasonable. The fast component represents a minor proportion of the type of carbons resonating in this signal, and as the temperature increases, the percentage of the fast component decreases steadily. It completely disappears above 90 °C (Figure 12b), a temperature which was previously proposed as a barrier for the oscillatory motions of the methylene chain.

Other signals which show an increase in T_{DD} as the temperature increases are the cis imine carbon (number 3 in Figure 1) and the nonprotonated aromatic carbon (as a function of the delay time to the power of 1) (number 4 in Figure 1). All other signals show either a scatter of data or a trend which cannot be interpreted in terms of motional relaxation.

Conclusions

A combination of chemical shift and relaxation information in variable-temperature CP-MAS ^{13}C-NMR spectra of PI10 gives a picture of this polymer dynamics. PI10 is synthesized as a combination of amorphous and crystalline phases. The crystalline phase contains cis and trans arrangements of the terephthalimine structure. The dominant motion at room temperature is the phenyl flips for the terephthalimine and some oscillatory movement of the methylene spacers. As the temperature increases, the frequency of the phenyl flips increases and surpasses 67.5 kHz at ca. 70 °C. The frequency of the methylene oscillations exceeds 67.5 kHz at a slightly higher temperature (ca. 90 °C). At T_{k-s} (ca. 107 °C), the cis structures

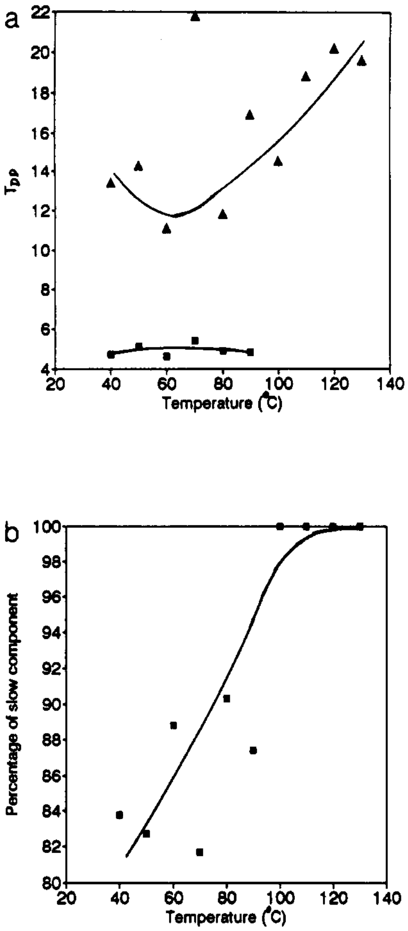


Figure 12. (a) T_{DD} as a function of temperature for peak 11 (Figure 1). (b) Percentage of the slow component as a function of temperature.

melt into the amorphous phase. From X-ray data, the trans structures are supposed to remain in the smectic G phase. There is no direct NMR evidence that the trans structures are still present. Also at T_{k-s}, the methylene chains, which are mostly in an all-trans conformation, start rotating to produce some gauche conformations. More gauche conformation in the methylene spacer starts appearing at the smectic–isotropic transition. Unfortunately, PI10 is not very stable at high temperatures, and this prevents more in-depth studies of PI10 dynamics at this transition. A $T_{1\rho C}$ measurement, for example, requires ca. 25 h, and the sample showed a significant brown coloration after the $T_{1\rho C}$ measurement at 130 °C.

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References and Notes

(1) Boeffel, C.; Spiess, H. W. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie: Glasgow, U.K., and London, 1989; p 224.
(2) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.
(3) Uryu, T.; Kato, T. *Macromolecules* **1988**, *21*, 378.
(4) Kato, T.; Kabir, G. M. A.; Uryu, T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1447.
(5) Kato, T.; Fujishima, A.; Uryu, T.; Matsushita, N.; Yamaguchi, H. *New Polym. Mater.* **1990**, *2*, 255.
(6) Perry, B. C.; Hahn, B.; Percec, V.; Koenig, J. L. *Polymer* **1990**, *31*, 721.
(7) Frech, C. B.; Adam, A.; Falk, U.; Boeffel, C.; Spiess, H. W. *New Polym. Mater* **1990**, *2*, 267.
(8) Yandrasits, M. A.; Cheng, S. Z. D.; Zhang, A.; Cheng, J.; Wunderlich, B.; Percec, V. *Macromolecules* **1992**, *25*, 2112.
(9) Natansohn, A.; Yang, H.; Clark, C. *Macromolecules* **1991**, *24*, 5489.
(10) Amundson, K. R.; Reimer, J. A.; Denn, M. M. *Macromolecules* **1991**, *24*, 3250.
(11) Chu, C. W.; Dickinson, L. C.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 201.
(12) Hatfield, C. R.; Aharoni, S. M. *Macromolecules* **1989**, *22*, 3807.
(13) Coppola, L.; Ranieri, G. A.; Chiellini, E.; Galli, G.; Veracini, C. A.; Angeloni, A. S.; Laus, M. *Polym. Commun.* **1991**, *32*, 5.
(14) Silvestri, R. L.; Koenig, J. L. *Macromolecules* **1992**, *25*, 2341.
(15) Yang, H.; Natansohn, A. *Macromolecules* **1992**, *25*, 5331.
(16) Yang, H.; Natansohn, A. *Macromolecules* **1992**, *25*, 5798.
(17) Yang, H.; Natansohn, A. *Polym. Bull.* **1992**, *29*, 159.
(18) Yang, H.; Natansohn, A. *Polymer*, in press.
(19) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.
(20) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.
(21) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. *Macromolecules* **1980**, *13*, 1121.
(22) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.
(23) Natansohn, A.; Yang, H., unpublished.
(24) Natansohn, A. *Chem. Mater.* **1992**, *4*, 182.
(25) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697.
(26) Cholli, A. L.; Ritchey, W. M.; Koenig, J. L.; Veeman, W. S. *Spectrosc. Lett.* **1988**, *21*, 519.